

*Express Letter*Remote detection of fumarolic gas chemistry at Vulcano, Italy,
using an FT–IR spectral radiometerToshiya Mori ^{a,*}, Kenji Notsu ^a, Yasunori Tohjima ^{a,1}, Hiroshi Wakita ^a,
P. Mario Nuccio ^b, Francesco Italiano ^c^a *Laboratory for Earthquake Chemistry, Faculty of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan*^b *Istituto di Mineralogia Petrografia e Geochimica, Università degli Studi, via Archirafi 36, 90123 Palermo, Italy*^c *Istituto di Geochimica dei Fluidi—CNR, via Torino 27/D, 90133 Palermo, Italy*

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Abstract

An infrared absorption spectroscopy remote sensing technique was used to determine the SO_2/HCl ratio in fumarolic plumes at **Vulcano**, Italy. The measurements were made from the southern crater rim of Fossa **Grande** Crater, about 400 m from the fumarolic area in the crater. Infrared absorption spectra of **HCl** and **SO**, were observed for four fumaroles a few tens of metres apart using the hot fumarolic surface as an infrared light source. The measured SO_2/HCl ratios in the FA, F47, FW and lower part of the F21 fumaroles were 4.5–5.4, 3.5, 9.5–11.2 and 5.8 respectively. The SO_2/HCl ratio of the FA fumarole was higher than that of the gas collected directly in the fumarolic vent (SO_2/HCl ratio = 2.9), and was closer to the $S_{\text{(total)}}/\text{HCl}$ ratio (= 4.6) of the collected gas. Our results show that the SO_2/HCl ratios of two fumaroles only a few tens of metres apart exhibits differences of about twofold. This suggests that this remote monitoring technique is capable of detecting spatial distribution in the SO_2/HCl ratios of volcanic plumes. Because temporal variations in S/Cl ratios can provide precursory signals for volcanic eruptions [1–31], this remote sensing technique can be used efficiently for evaluation of volcanic activity.

1. Introduction

Remote analysis of volcanic gas plumes using infrared absorption spectroscopy was first attempted by Naughton et al. [4] during their pioneering work at Kilauea volcano. These authors observed the ab-

sorption spectrum of a volcanic plume using infrared emission from a lava fountain as the light source. However, it is only in recent years that technological developments in FT–IR spectroscopy [5] have allowed the use of portable instruments on volcanoes. Recently, Mori et al. used remote FT–IR spectrometry at Unzen volcano (Japan) [6] to measure the SO_2/HCl ratios in volcanic plumes. During the Unzen experiment, the infrared absorption spectra of volcanic gases were observed from a point located about 1300 m from the hot lava dome, which was

* Fax +81-3-3816-1784; e-mail mori@eqchem.s.u-tokyo.ac.jp

¹ Now at: National Institute for Environmental Studies, Onogawa, Tsukuba City, Ibaraki 305, Japan.

used as a light source. (An adequate light source must be available to observe absorption by volcanic species such as HCl with this remote sensing method. The availability of light is the most serious limitation encountered in using a natural infrared light source, because the number of active lava domes and lava fountains is small.)

In order to increase the potential of the method, we attempted to apply remote FT-IR measurements to fumarolic areas, as these are common at many volcanoes. In this paper we report the results obtained on Vulcano Island, Italy, where we used the hot ground surface of some fumaroles (several hundred degrees Celsius) as an infrared light source.

2. Measurements at Vulcano

Vulcano is located off the northern coast of Sicily (Fig. 1), and has not erupted since 1888–1890. Today, the fumarolic activity is especially intense on the northern internal flank and rim of the Fossa Grande Crater (Fig. 1) [7,8]. Since the end of 1977, the fumarolic area has expanded and the highest temperature of the gases has increased [8,9]. The maximum temperature of the fumarolic gases until 1987 was 315°C, but it reached 690°C early in 1993, and has since declined to 540°C [10].

The instrumental system used for the measurements is the same as that described in our work at Unzen [5], and is composed of three parts: a Cassegrainian-type telescope (field of view = 5 mrad), an FT-IR spectral radiometer, and a computer. The FT-IR spectral radiometer was set to a spectral resolution of 1 cm⁻¹ and a MCT (mercury cadmium tellurium) detector was cooled by liquid nitrogen to 77 K. Observations were made on April 24, 1993. The instrument was placed on the southern crater rim of Fossa Grande Crater, 355 m above sea level, where the fumaroles in the crater were clearly visible. From among many in the crater we observed four fumaroles (FA, F47, F21 and FW, Fig. 1). In April 1993 the FA fumarole located, halfway up the northern internal flank, was the largest (about 470 m²) and hottest [10]. The F21 fumarole is narrow (a few metres wide) and runs up the internal flank from the bottom of the crater for about 30 m. The distance between the FA and FW fumaroles was about 40 m and that between the FW and the lower part of F21 fumarole was about 30 meter. The observation site was located on the opposite crater rim part, about 410 m, 380 m and 365 m, respectively, from the central part of FA, FW and the lower part of F21.

At a distance of about 400 m the field of view of the instrument was about 2 m. Measurements were made by aiming the telescope at the target spot and

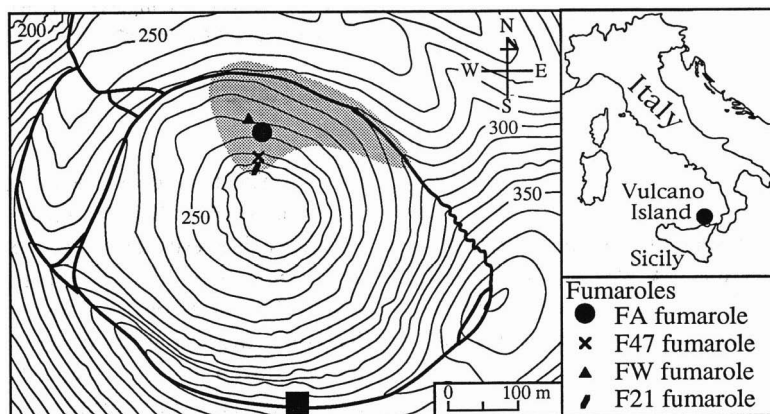


Fig. 1. Map of the Fossa Grand Crater showing the observation site (■) on the southern crater rim and the observed fumaroles on the northern inside slope of the crater. The shaded area corresponds to the fumarolic zone at Fossa Grande Crater. The bold curves shows the paths; a large loop in the paths coincides with the crater rim of Fossa Grande Crater.

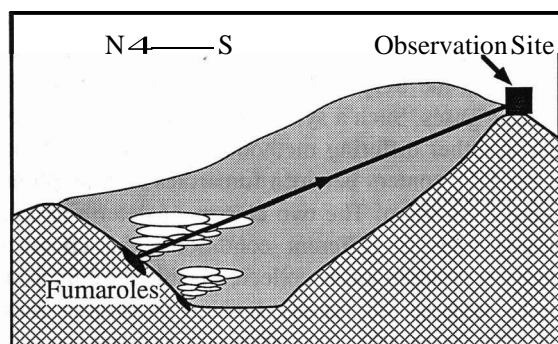


Fig. 2. Schematic cross section of FT-IR observation conditions at Fossa Grande Crater. The instruments were settled on the southern crater rim of Fossa Grande Crater and aimed downwards at the fumaroles on the northern internal slope of the crater. Measurements were carried out using infrared radiation from the high-temperature surface of the fumaroles and observed infrared absorption of SO_2 and HCl in the fumarolic plume emanating from the target fumaroles.

observing the gas plume emanating from that point (Fig. 2). The time required to obtain one infrared spectrum was about 4 min.

3. Results

Eleven infrared spectra were obtained at the crater rim. Five spectra were measured aiming at the central part of the FA fumarole and four spectra at the FW fumarole. One spectrum was for the lower part of F21 fumarole and F47 fumarole. Fig. 3 shows a typical infrared spectrum. Absorption features of SO_2 (ν_1) and HCl were identified in all eleven observed spectra. Absorption features of SO_2 and HCl can be distinguished from those of water vapour in the atmosphere in the wavenumber ranges 1100–1200 cm^{-1} and 2750–2900 cm^{-1} respectively (Fig. 3). The signal-to-noise ratios of the observed spectra are roughly estimated at 50 for 1100–1200 cm^{-1} and 10 for 2750–2900 cm^{-1} . In spectral analyses, the radiance perceived by the spectral radiometer $P(\nu)$ was expressed as the following simple equation:

$$P(\nu) = P_0(\nu)\tau(\nu) + P_1(\nu)$$

where ν represents wavenumber (cm^{-1}), $P_0(\nu)$ represents the radiance (mostly from the fumarolic surface), $P_1(\nu)$ represents the ambient radiance at the

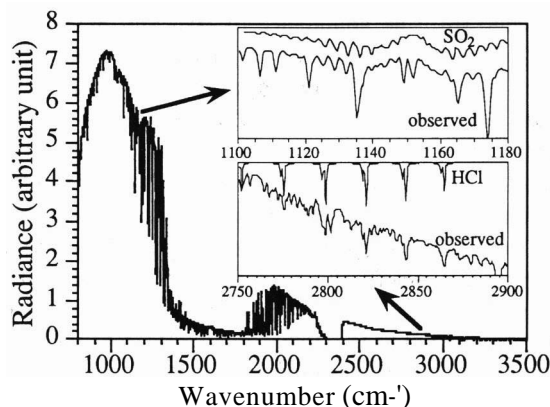


Fig. 3. Typical FT-IR spectrum of the fumarolic plume of the FA fumarole on April 23, 1993. The upper inset shows the observed spectrum (lower spectrum) and absorption features of SO_2 (upper spectrum) in the wavenumber range 1100–1200 cm^{-1} . The lower inset shows the observed spectrum (lower spectrum) and absorption features of HCl (upper spectrum) in the wavenumber range 2750–2900 cm^{-1} . Absorption features of SO_2 and HCl clearly appear in the observed spectrum in both wavenumber ranges.

instrument, and $\tau(\nu)$ represents the infrared spectral transmittance of the atmosphere including the fumarolic plume.

The spectral analysis method applied to calculate the amount of SO_2 and HCl in the air column is the same as that used in our previous work at Unzen

Table 1

SO_2/HCl ratios in the fumarolic plume from Vulcano on April 24, 1993

Spectrum No.	start time of measurements	SO_2/HCl Ratios	Target Fumaroles
1	15:45	3.5 ± 0.9	F47
2	16:03	11.2 ± 3.5	FW
3	16:11	4.5 ± 1.2	FA
4	16:17	4.6 ± 1.2	FA
5	16:49	9.8 ± 2.7	FW
6	16:54	9.5 ± 2.5	FW
7	17:01	9.5 ± 2.5	FW
8	17:19	4.9 ± 1.3	FA
9	17:23	5.4 ± 1.5	FA
10	17:29	5.3 ± 1.4	FA
11	17:35	5.8 ± 2.7	Lower F21

volcano [6]. The abundance of HCl and SO₂ in the air column intersected by the telescope was calculated using wavenumber ranges of 1110–1134 cm⁻¹ and 1140–1170 cm⁻¹ for the SO₂ analyses and 2810–2870 cm⁻¹ for the HCl analyses. SO₂/HCl ratios in the fumaroles were obtained by dividing the column amounts of SO₂ by the column amounts of HCl calculated from the same spectra. The errors in Table 1 are mainly due to uncertainties in the instrumental line shape, zero level offset, and temperature. The calculated SO₂/HCl ratios for the FA, F47, FW and lower F21 fumaroles are 4.5–5.4, 3.5, 9.5–11.2 and 5.8 respectively (Table 1).

4. Discussion

Because chemical compositions of fumarolic gases collected at the time of remote measurement are not available, we have compared our results with chemical data from the nearest date. The SO₂, H₂S and HCl contents and fumarolic temperature of the FA fumarole, collected on April 23, and those of F47, FW and the lower F21, collected on May 27, are shown in Table 2.

The SO₂/HCl ratios determined by our FT-IR remote measurements are significantly and systematically higher than those displayed by chemical analyses of the fumarolic gases. In particular, the SO₂/HCl ratios of the FA fumarole measured by FT-IR showed values closer to the (SO₂ + H₂S)/HCl ratios of the analyzed gas, which was collected one day before. It is worth noting that SO₂ fluxes from Vulcano's fumaroles, measured remotely with COSPEC [11,12] and DIAL [13], gave values that

were generally higher than the estimates based on scaling the steam output measured at fumaroles [14,15] to the SO₂/H₂O concentration ratios of fumarolic gases. Such a systematic discrepancy may be due to either differing methods or actual differences in the SO₂ content between fumaroles and the plume rising from them. The two classes of determinations indeed refer to different conditions: the chemical analyses concern gases collected inside the fumarolic vents, whereas all remote sensing techniques measure the gases after their emission and mixing with air. Thus we must consider the possible chemical and physical phenomena affecting the gases after their release from the fumarole into the atmosphere:

(1) *Deposition of elemental sulphur (2H₂S + SO₂ = 3S + 2H₂O) [16].* Reactions between sulphur compounds of fumarolic plumes would lead to SO₂ consumption and a consequent lowering of the SO₂/HCl ratio compared to its value in the vent. Because higher, not lower, ratios were measured by FT-IR, this process can be dismissed.

(2) *Different partitioning of SO₂-HCl into condensed steam (liquid droplets) of plumes.* According to calculations using thermodynamic constants at 25°C [17,18], HCl would partition into liquid droplets about a million times more than SO₂, with a consequent increase in the SO₂/HCl ratio. The discrepancies we observed are far smaller, but this process is the most efficient in explaining the discrepancies. We do not know how this dissolution process actually occurs in the fumarolic plume of Vulcano.

(3) *Rapid oxidation of H₂S to SO₂ in the plume.* Rapid oxidation of H₂S to SO₂ has been reported at Mt. St. Helens [19] and Mt. Erebus [20], although estimates of the mean lifetime of H₂S oxidation vary

Table 2
S and Cl contents in gases collected in the fumarolic vents of Vulcano (vol%)

Fumarole No.	Date of Sampling				SO ₂ /HCl	S _{total} /HCl*	Temp.
		SO ₂	H ₂ S	HCl	Ratios	Ratios	(°C)
FA	Apr. 23, 1993	0.32	0.18	0.11	2.9	4.6	666
F47	May 27, 1993	0.84	0.62	0.36	2.3	4.1	490
Lower F21	May 27, 1993	0.81	0.62	0.37	2.2	3.9	440

* S_{total}/HCl = (SO₂ + H₂S)/HCl

widely, suggesting that the kinetics of oxidation strongly depend on the environment conditions [21–23]. Furthermore, combustion of H_2S may occur at Vulcano, as the temperature of almost all fumaroles is above the minimum autocombustion temperature of H_2S (290°C) [24]. Airborne measurements in the Vulcano plume in 1984 [11] yielded fluxes of 25 t/day for SO, and 20 t/day for H_2S (i.e., a $\text{H}_2\text{S}/\text{SO}_2$ molar ratio of about 1.5, which is consistent with the contemporaneous analysis of the fumaroles at the crater). This result suggests that the oxidation of H_2S is not a rapid process at Vulcano. However, because the fumarolic gas temperature (Table 2) is clearly higher than the maximum 1984 fumarolic temperature of about 300°C [9], the rapid oxidation process cannot be entirely dismissed.

(4) *Interference of gases from other fumaroles.* At Vulcano the SO_2/HCl ratios vary significantly from fumarole to fumarole [8] and, although we assume that the origin of the observed HCl and SO, is only due to the gas of the target fumarole, we cannot completely exclude the possibility that the gases emitted from other fumaroles occasionally intersect the optical column of the FT–IR.

Different fumaroles that lie tens of metres apart from each other and which are measured by FT–IR (Table 1) show different SO_2/HCl ratios. The ratio of the FW fumarole is nearly twice as high as that of FA, F47 and the lower part of F21. This difference in observed ratio is considered as a real chemical feature at the respective fumaroles, although we will have to consider the process of atmospheric mixing in further studies. Chiodini et al. [8] suggest that the spatial and temporal variations in the acid content of fumaroles can be explained by the mixing of a unique deep magmatic component and two shallow hydrothermal components. They also suggest that the differences in the acid content of shallow hydrothermal components reflect differences in the physical variables controlling hydrolysis reactions involving salts and silicate rocks [8]. Therefore, the observed difference in the SO_2/HCl ratios of the fumaroles should reflect such differences.

Seeing as temporal changes in S/Cl ratios in volcanic and fumarolic gas are potential precursors of volcanic eruptions [1–3], FT–IR remote sensing techniques may be efficiently used for the monitoring of volcanic and fumarolic activity. In particular

at Vulcano, where many fumaroles exist, both spatial and temporal changes in the fumarolic activity may be monitored using this remote monitoring technique.

5. Conclusion

(1) Remote FT–IR measurements of SO_2/HCl ratios in fumarolic plumes were carried out at Vulcano, Italy. The high-temperature ground surface of the fumarolic area was used as a light source for the remote infrared absorption measurements of HCl and SO, in the volcanic plume.

(2) The SO_2/HCl ratios for most fumaroles remotely determined with FT–IR are systematically higher than the ratios of gases collected in the fumarolic vents, and are closer to the $\text{S}_{(\text{total})}/\text{HCl}$ ratio. This discrepancy may result from chemical and physical processes in the fumarolic plumes.

(3) The SO_2/HCl of two fumaroles (FA and FW), which are a few tens of metres apart from each other, showed a difference of about twofold. This remote monitoring technique is thus capable of detecting compositional differences in volcanic fumaroles, and provides much faster information than conventional sampling and analytical methods.

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References

- [1] F. Tonani, Concepts and techniques for geochemical forecasting of volcanic eruptions, in: *The Surveillance and Prediction of Volcanic Activity: A Review of Methods and Techniques* (Earth Sciences 8), pp. 145–166, UNESCO, Paris, 1971.
- [2] LA. Menyailov, Prediction of eruptions using changes in composition of volcanic gases, *Bull. Volcanol.* 39, 112–125, 1975.

- [3] J. Hirabayashi, J. Ohsaka and T. Ozawa, Relationship between volcanic activity and chemical composition of volcanic gases—a case study on Sakurajima volcano, *Geochem. J.* 16, 11–21, 1982.
- [4] J.J. Naughton, J.V. Derby and R.B. Glover, Infrared measurements on volcanic gas and fumes: Kilauea eruption, 1968, *J. Geophys. Res.* 74, 3273–3277, 1969.
- [5] L.R. Brown, C.B. Farmer, C.P. Rinsland and R. Zander, Remote sensing of the atmosphere by high resolution infrared absorption spectroscopy, in: *Spectroscopy of the Earth's Atmosphere and Interstellar Medium*, K.N. Rao and A. Weber, eds., pp. 97–151, Academic Press, Boston, 1992.
- [6] T. Mori, K. Notsu, Y. Tohjima and H. Wakita, Remote detection of HCl and SO₂ in volcanic gas from Unzen volcano, Japan, *Geophys. Res. Lett.* 20, 1355–1358, 1993.
- [7] L. Bolognesi and F. D'Amore, Isotopic variation of the hydrothermal system on Vulcano Island, Italy, *Geochim. Cosmochim. Acta* 57, 2069–2082, 1993.
- [8] G. Chiodini, R. Cioni and L. Marini, Reactions governing the chemistry of crater fumaroles from Vulcano Island, Italy, and implications for volcanic surveillance, *Appl. Geochem.* 8, 357–371, 1993.
- [9] M. Martini, Water and fire: Vulcano island from 1977 to 1991, *Geochem. J.* 27, 297–303, 1993.
- [10] P. Bonfanti, F. Italiano, P.M. Nuccio, G. Pecoraino and E. Principio, Attivita' esaltativa al cratere di Vulcano, *GNV–CNR Annu. Meet. (Rome, 8–10 June 1993)*, p. 251, 1993 (Abstr.).
- [11] P. Allard, N. Bruno, T. Caltabiano, J. Carbonnelle, H. Loyer and R. Romano, COSPEC survey of the sulfur dioxide output from Vulcano in 1984–1993: Volcanological and methodological implications, *WOVO Workshop (Guadeloupe, 13–17 December 1993)*, Program Abstr., 1993.
- [12] T. Caltabiano and R. Romano, COSPEC measurements of SO₂ flux from Vulcano crater, in: *Unrest at Vulcano, GNV–CNR Annu. Meet. (Rome, 8–10 June 1993)*, p. 139, 1993 (Abstr.).
- [13] H. Edner, P. Ragnarson, S. Svanberg, E. Wallinder, R. Ferrara, R. Cioni, B. Raco and G. Taddeucci, Total fluxes of sulfur dioxide from the Italian volcanoes Etna, Stromboli and Vulcano measured by differential absorption lidar and passive differential optical absorption spectroscopy, *J. Geophys. Res.* 99, 18827–18838, 1994.
- [14] F. Italiano and P.M. Nuccio, Volcanic steam output directly measured in fumaroles: the observed variations at Vulcano island, Italy, between 1983 and 1987, *Bull. Volcanol.* 54, 623–630, 1992.
- [15] M. Valenza, Vulcano geochemistry, *Bull. Volcanol. Eruptions* 29, 91–94, 1992.
- [16] S. Matsuo, Establishment of chemical equilibrium in the volcanic gas obtained from the lava lake of Kilauea, Hawaii, *Bull. Volcanol.* 24, 59–71, 1962.
- [17] I. Barin, *Thermochemical Data for Pure Substances*, 2nd ed., VCH, Weinheim, 1993.
- [18] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney and R.L. Nuttall, The NBS tables of chemical thermodynamic properties—selection for inorganic and C, and C, organic substances in SI units, *J. Phys. Chem. Ref. Data* 11(Suppl. 2), 1982.
- [19] T.J. Casadevall and L.P. Greenland, The chemistry of gases emanating from Mount St. Helens, May–September 1980, *U.S. Geol. Surv. Prof. Pap.* 1250, 221–226, 1981.
- [20] G. Zreda-Gostynska, P.R. Kyle and D.L. Finnegan, Chlorine, fluorine, and sulfur emissions from Mount Erebus, Antarctica and estimated contributions to the Antarctic atmosphere, *Geophys. Res. Lett.* 20, 1959–1962, 1993.
- [21] W. Jaeschke, H. Berrensheim and H.W. Georgii, Sulfur emissions from Mt. Etna, *J. Geophys. Res.* 87, 7253–7261, 1982.
- [22] S.A. Penkett, Oxidation of SO₂ and other atmospheric gases by ozone in aqueous solution, *Nat. Phys. Sci.* 240, 105–106, 1972.
- [23] D.J. Spedding and D.M. Cope, Field measurements of hydrogen sulphide oxidation, *Atmos. Environ.* 18, 1791–1795, 1984.
- [24] R. Faivre-Pierret and F. Le Guem, Health risks linked with inhalation of volcanic gases and aerosols, in: *Forecasting Volcanic Events*, H. Tazieff and J.C. Sabroux, eds., pp. 69–81, Elsevier, Amsterdam, 1983.